Novel Ion-Containing Reverse Osmosis Membranes. I. Preparation and Selected Properties

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Synopsis

Grafting and subsequent quaternization of 2- and 4-vinylpyridine to poly(vinyl chloride) (PVC) and to poly[3,3-bis(chloromethyl)oxetane], Penton, films have been exploited to prepare novel ion-containing membranes. 2-Vinylpyridine-grafted "Penton" films are the most attractive system for further study since the PVC grafts were unstable under the requisite extraction conditions. Although the sterically less hindered 4-vinylpyridine-grafted films were easier to quaternize, weight gain calculations indicated that complete quaternizations were only achieved with the 2-vinylpyridine-grafted films. High ionic concentrations were obtained in the grafted membranes. The mechanical properties of the wet films were measured. Salt absorption studies demonstrated that significant salt exclusion was achieved at relatively high salt concentrations although the grafted films sorbed up to 30 vol % water.

INTRODUCTION

Ion-containing reverse osmosis membranes were prepared by grafting nonionic monomers to stable polymer substrates followed by a suitable reaction designed to confer ionic character to the grafted chains. Stannett et al.[1,2] have indicated previously that grafting followed by an ion-forming reaction is an attractive alternative to direct grafting of ionic monomers or direct chemical modification of the base polymer. Grafting and subsequent ion formation avoids using inherently expensive monomers.[3] Moreover, polymer damage often attends direct chemical modification of base polymers. Interesting properties of the ion-containing grafts include the combination of the good mechanical properties of a strong substrate and hydrophilic behavior derived from the ionic character of grafted chains.

In this study 2-vinylpyridine (2-VP) and 4-vinylpyridine (4-VP) were grafted to poly(vinyl chloride) (PVC) and poly[3,3-bis(chloromethyl)oxetane], Penton. After the grafting step, ionic character was introduced to the grafted chain by quaternization with methyl bromide. In part I, here, the grafting protocols and selected properties are presented. The 2-VP-grafted Penton films were the most stable and reproducible, and therefore most of the characterization focused on these preparations. The reverse osmosis properties of such films will be described in detail in part II of this article.

EXPERIMENTAL

Grafting was conducted on 1- and 1.5-mil commercial (Hoechst Co., W. Germany) unplasticized PVC films. Penton films were cast from hot dimethylformamide solutions containing 12% by weight of polymer. The polymer was

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obtained in granule form from the Hercules Co. The cast films were clear and uniform as indicated by density measurements made on a density gradient column; the average density was 1.402. The monomers used were distilled before use. Grafting was conducted using a ^{60}Co gamma cell with a dose rate of 0.85 Mrad/hr using degassed glass ampoules containing the film to be grafted, monomer, methanol, and dimethylformamide. A second grafting method, which eliminated the use of closed glass ampoules, was used where the films were grafted in a nitrogen atmosphere with a small positive pressure of nitrogen gas flowing through a steel container exposed to the radiation.

After irradiation, hydroquinone was used to stop the reaction. Extraction of homopolymer was conducted by Soxhlet extraction using methanol as the extracting solvent.

Quaternization was carried out in closed glass ampoules where the grafted films were exposed to an excess of methyl bromide.

RESULTS AND DISCUSSION

Both PVC and Penton were used as substrates because of their good mechanical properties. Both 2-VP and 4-VP were used in order to compare their behavior with respect to grafting and quaternization. It was expected that 4-VP would present less steric hindrance to quaternization, resulting in faster reaction and higher yields. A detailed study of the kinetics of grafting was not intended nor undertaken in this work. The effect of ionizing radiation on PVC has been studied in detail, and an abundant collection of those studies is described by Chapiro.[4] It was pointed out by Chapiro that the expected $G(R^0)$ value, i.e., the number of radicals per 100 eV of absorbed radiation of PVC, using a model low-molecular-weight allyl chloride, should be 10–15, which is a relatively high value. The G values for gas production, mainly hydrogen chloride, have been determined by different workers and show considerable variation (0.25–22.6). Results of reverse osmosis properties of radiation-grafted PVC films were recently studied by Stannett et al.[2] A recent ESR study of PVC films gave a G(radical) value[5] of 4.6. ESR studies of gamma-irradiated Penton films have also been conducted, by Chung et al.[6] A total G value for two radical species was found to be 0.8.

High grafting yields were obtained both with PVC and with Penton films as shown by the grafting curves in Figures 1 and 2. 4-Vinylpyridine gave consistently higher yields than 2-vinylpyridine. The reason for this is not clear since the propagation rate constants are consistently somewhat higher for the 2-vinyl monomer; it is possible, however, that the swelling is different for the two monomers. The grafting yields shown in Figures 1 and 2 were conducted after degassing under high vacuum. However, as shown in Figure 2, grafting in a slowly flowing nitrogen atmosphere gave similar yields under much more practical conditions. The dry grafted PVC films were quite brittle and had to be handled with care but were stronger when wet. The grafted Penton films, on the other hand, remained strong and tough.

The effect of extraction time on the calculated percent grafting of Penton films is shown in Figures 3 and 4. As shown by Figure 3, the weight loss of 2-VP-grafted films stabilized within four days of extraction while 4-VP grafted films continuously lost weight. The reason for this is not clear; it could be due to the

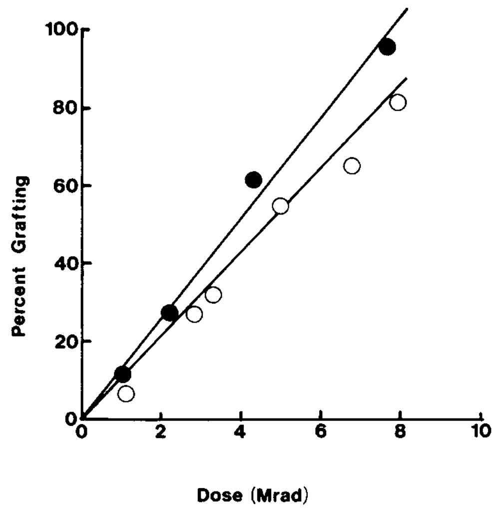

Fig. 1. Effect of dose on the percent grafting of 1 mil PVC films. Grafting solution, 30/70 volume parts of monomer to methanol; (○) 4-VP; (●) 2-VP. Dose rate 0.55 Mrad/hr. Under vacuum.

greater ease of extraction or more occlusion of homopolymer in the case of 4-VP. In any case the greater stability of the 2-VP-grafted films made them much more attractive for the subsequent detailed studies including their reverse osmosis behavior.

The various grafted films were then quaternized. Initial studies with methyl bromide showed that the 2-VP- and 4-VP-grafted PVC films darkened and lost weight continuously with methanol extraction and changed their color to deep

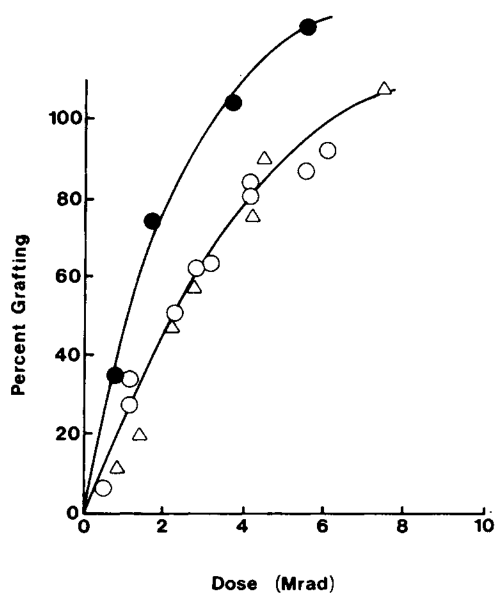

Fig. 2. Effect of dose on the percent grafting of 1.5-mil Penton films. Grafting solution, 20/30/50 volume parts of monomer/methanol/dimethylformamide; (○) 4-VP in vacuum; (△) 2-VP under vacuum; (●) 2-VP under nitrogen. Dose rate 0.55 Mrad/hr.

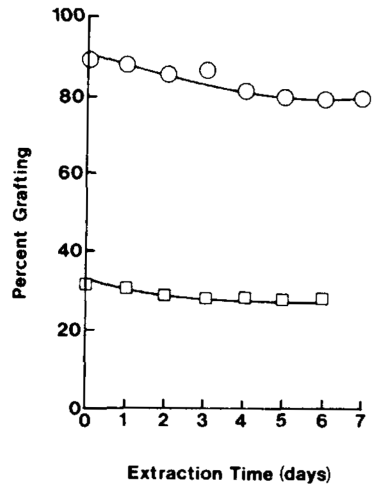

Fig. 3. Effect of Soxhlet extraction time on the calculated percent grafting of Penton films grafted with 2-VP. Solvent, methanol; (△) dose 5.6 Mrad; (□) dose 1.4 Mrad.

blue. It was decided to use the 2-VP-grafted Penton films in the quaternization studies because of the stability of this system and the lack of color changes.

The quaternization of poly-2-VP and poly-4-VP has been investigated by Fuoss and Strauss[7] and Strauss and Jackson.[8] The former workers quaternized poly-4-VP with *n*-butyl bromide using nitromethane as solvent, obtaining yields of approximately 95%. The latter group conducted viscosity and solubilization studies of poly-2-VP quaternized with *n*-dodecyl bromide using nitromethane as solvent resulting in only 33.7% of the nitrogen quaternized. A higher degree of quaternization was reported when poly-4-VP was used instead.

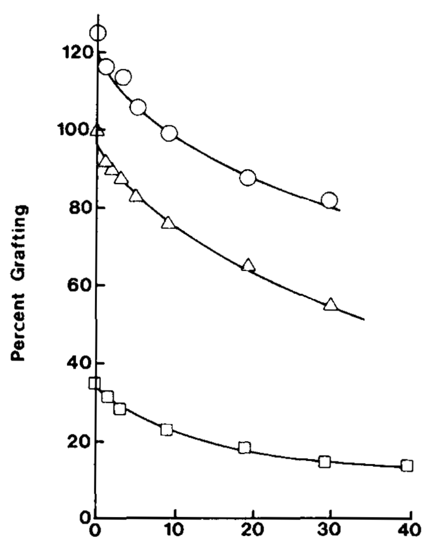

Fig. 4. Effect of Soxhlet extraction time on the calculated percent grafting of Penton films grafted with 4-VP. Solvent, methanol; (○) dose 6.4 Mrad, (△) dose 3.7 Mrad; (□) dose 2.7 Mrad.

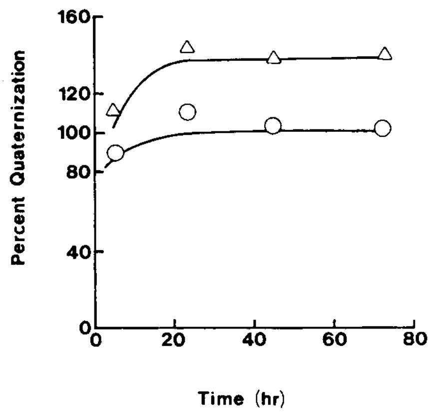

Fig. 5. Effect of time on percent quaternization of Penton films grafted with 29% 2-VP calculated before washing with water (△) and after washing with water (○). Quaternization agent, methyl bromide at 60°C.

Preliminary experiments conducted in this work indicated that it was relatively easier to quaternize grafted poly-4-VP chains. The same yield was obtained at 25, 40, and 60°C while the yield of quaternization of grafted poly-2-VP was strongly dependent on temperature. The 4-VP-grafted systems, however, were not explored further owing to the problems of instability to the extraction method used discussed earlier.

The effect of reaction time on the percent quaternization of Penton films grafted with poly-2-VP is shown in Figures 5 and 6. The upper curves were obtained with calculations based on the weight gains of films after quaternization and drying to constant weight in a vacuum oven; the calculated percent quaternizations were higher than the theoretical maximum of 100%. After the films were immersed in water, however, and again dried in a vacuum oven, the calculated quaternization was reduced to very close to 100%. It was postulated that the weight loss was due to methyl bromide tenaciously held in the rigid films which was later released by swelling. Quaternization attempts with ethyl bromide and dimethyl sulfate failed owing to the choice of solvent (methanol), and

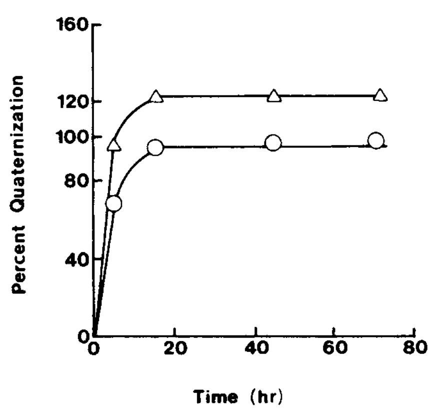

Fig. 6. Effect of time on percent quaternization of Penton films grafted with 80% 2-VP calculated before washing with water (△) and after washing with water (○). Quaternization agent, methyl bromide at 60°C.

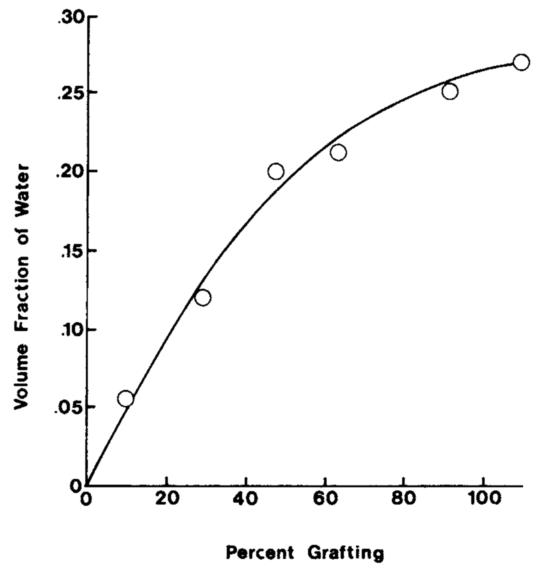

Fig. 7. Volume fraction of water of Penton films grafted with 2-VP and quaternized with methyl bromide.

the weight gains were completely lost after the film was washed with water. This was probably due to alcoholysis of the quaternization agents. Fuoss and Strauss[7] reported that attempts to quaternize poly-4-VP with n-butyl bromide using alcohols as solvents led to alcoholysis of the n-butyl bromide with high contamination of hydrogen bromide. Complete details of the extensive grafting and quaternization studies may be found in ref. 9.

Quaternization of the grafted chains results in films that swelled considerably in water. The water sorption of Penton films grafted to different extents is shown in Figure 7. It is interesting to note that the number of water molecules (Table I) per ionic site is fairly constant and close to what should be expected as hydration water of the cation and the anion, and limited probably by the elastic force generated by the change of entropy of the polymeric chains in the amorphous zone of this semicrystalline polymer. In this case the crystallites work as crosslinking sites. Relatively high concentrations of fixed ionic sites were achieved, as shown by Figure 8. This high concentration is desirable inasmuch

TABLE I
Number of Water Molecules Absorbed per Ionic Site in 2-VP-Grafted Penton Membranes Quaternized with Methyl Bromide

Percent grafting	Molecules H_2O per ionic site
10.0	7.12
29.0	5.0
47.2	7.19
57.0	7.19
62.0	6.30
80.0	7.36
83.0	7.36
92.5	7.84
109	7.12

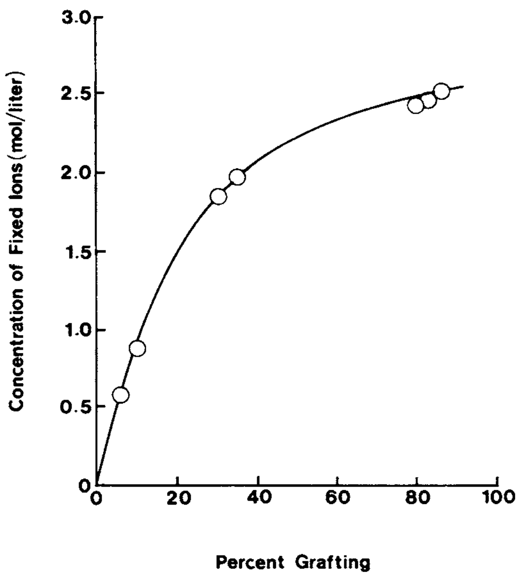

Fig. 8. Specific concentration of fixed ions of hydrated 2-VP-grafted membranes quaternized with methyl bromide.

as the membrane rejection of ionic solutes depends on the relative concentration of charges on the membrane and the solution.

The salt sorption of a Penton membrane grafted with 80% 2-VP and quaternized with methyl bromide was studied using neutron activation analysis. The concentration of sodium C_{+m} in the membrane with a concentration of X fixed charges per unit volume is given by the well-known equation[10]

$$C_{+m} = -\frac{X}{2} + \left[\left(\frac{X}{2}\right) + \left(\frac{\gamma\pm}{\gamma\pm_m} C_s\right)^2\right]^{1/2} \tag{3}$$

where $\gamma\pm$ and $\gamma\pm_m$ are, respectively, the activity coefficients of the solute in the solution and in the membrane; and C_s is the concentration of salt in solution. Rigorously, the activity ratio in the formula above should contain the effect of swelling pressure given by the contractive forces of the polymer network. The concentration of fixed charges based on the total volume of the swollen membrane was 2.4 mole/l. Using this value for X in the equation above and the measured concentrations of sodium in the membrane exposed to different concentrations of sodium chloride, the ratio $\gamma\pm/\gamma\pm_m$ was determined for each concentration. As shown by Table II, there is a tendency for the ratio of the activity coefficients to increase as the external salt concentration is decreased. As pointed out by Helferich,[11] this tendency, often observed experimentally, is attributed to non-Donnan types of absorption and to experimental errors.

The tensile properties of the wet membranes were tested after being equilibrated with water. Tests were conducted with an Instron machine at 20°C and with a constant strain rate of 8.3%/sec. Values for mechanical properties of unmodified Penton films have been given by Sandiford[12] as 6×10^3 for tensile strength, 10% for strain at failure, and 1.7×10^5 psi for initial modulus. These measurements were made at 20°C. In this work, corresponding values for the ungrafted Penton were, respectively, 4×10^3, 7.4%, and 2×10^5 psi. The minor

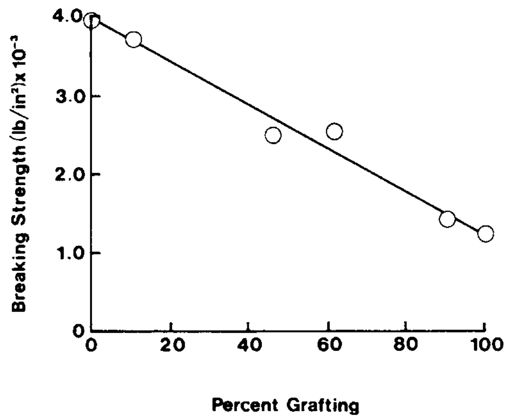

Fig. 9. Breaking strength of wet Penton films grafted with 2-VP and quaternized with methyl bromide.

differences may be explained by the fact that the films used in this work were equilibrated with water and probably had somewhat different degrees of crystallinity.

The effect of grafting and quaternization and the consequent increase in the absorption of water on the mechanical properties, shown in Figures 9, 10, and 11, is similar in character to the effects of adding a plasticizer to a polymer. The initial modulus and breaking strength decreased markedly while the extension at break curve showed a maximum. The initial modulus decreased by an order of magnitude. For the more highly quaternized membranes, compaction could become significant at the pressure differences used in reverse osmosis.

In summary, it can be said that the grafting and quaternization of 2-VP to Penton resulted in membranes that retained good mechanical properties and contained high concentrations of ionic sites. These are desirable characteristics for membranes used in reverse osmosis where compaction is to be avoided and where the high concentration of ionic sites results in high salt rejection at relatively high salt concentrations.

The quaternization studies indicated that close to 100% yields could be obtained, while from the literature it was not always clear that such degrees of quaternization were actually achieved in similar work.

It should be pointed out that the average number of water molecules per ionic site in the membranes was approximately 7, which is close to what one should

TABLE II
Effect of External Salt Concentration on Sorption of Salt by Penton Membranes Grafted with 80% 2-VP and Quaternized with Methyl Bromide[a]

C_s, mole/l.	C_m, mole/l.	C_m/C_s	$\lambda\pm/\lambda\pm_m$[b]
0.8620	0.082	0.095	0.530
0.5172	0.0475	0.0918	0.667
0.0862	0.0061	0.0707	1.462
0.0172	0.0074	0.043	2.626

[a] Measured at 25°C. C_s and C_m are concentrations of NaCl in solution and membrane, respectively.
[b] Ratio of activity coefficients in the solution and membrane.

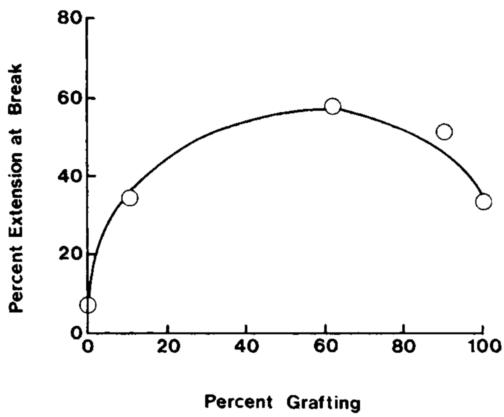

Fig. 10. Percent elongation at break of wet Penton films grafted with 2-VP and quaternized with methyl bromide.

expect as water of hydration of the ionic pair. This suggests that the elastic forces of the matrix are strong enough to limit the water absorption to the most strongly bound molecules. Physically, this may mean that ions passing through the membranes might have to borrow some of the water molecules as they diffuse through the membrane, thus facing a energy barrier which should result in higher salt rejections.

Using the literature values for the densities of amorphous and crystalline Penton,[12] the calculated crystallinity of films was around 19%. This degree of crystallinity and the ungrafted areas of the polymers were apparently enough to act as massive "crosslinks" which created retractive forces to oppose hydration. Other systems which do not offer such resistance may absorb water above this more closely bound shell, resulting in lower ionic concentrations and lower rejections and mechanically weaker membranes.

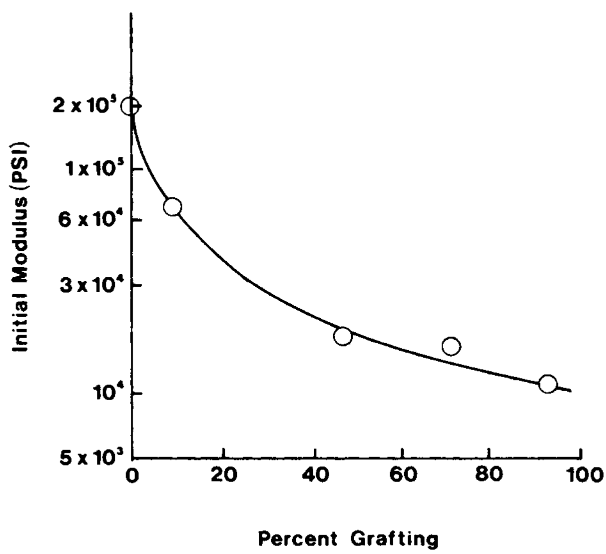

Fig. 11. Initial modulus of wet Penton films grafted with 2-VP and quaternized with methyl bromide.

This article summarizes a rather extensive and detailed study of the preparation of vinylpyridine-grafted PVC and Penton films and of the subsequent quaternization studies. Full details may be found in ref. 9. The reverse osmosis properties of the films are presented in refs. 9 and 13.

References

1. V. Stannett, H. B. Hopfenberg, E. Bittencourt, and M. I. Haider, Grafted Membranes for Reverse Osmosis, in *Reverse Osmosis and Synthetic Membranes,* S. Souirajan, Ed., National Research Council, Canada, Ottawa, Canada, 1977.

2. V. Stannett, H. B. Hopfenberg, F. Kimura-Yeh, and J. L. Williams, in *Polyelectrolytes and their Applications,* E. Selegny and A. Rembaum, Eds., Reidel, Dordrecht, Holland, 1975, pp. 235–247.

3. M. F. Hoover and G. B. Butler, *J. Polym. Sci., Polym. Symp.,* **45,** 1 (1974).

4. A. Chapiro, *Radiation Chemistry of Polymeric Systems,* Interscience, New York, 1962, Chap. 12.

5. K. Mitri, E. P. Stahel, T. Memetea, and V. Stannett, *J. Macromol. Sci. Chem.,* **22,** 337 (1977).

6. Y. J. Chung, D. R. Squire, and V. T. Stannett, *J. Macromol. Sci. Chem.,* **8,** 1403 (974).

7. R. M. Fuoss and U. P. Strauss, *J. Polym. Sci.,* **3,** 246 (1948).

8. U. P. Strauss and E. G. Jackson, *J. Polym. Sci.,* **6,** 649 (1951).

9. E. Bittencourt, Ph.D. thesis, North Carolina State University, 1976.

10. U. Merten, in *Desalination by Reverse Osmosis,* M.I.T. Press, Cambridge, MA 1966, Chap. 2.

11. F. Hellfrich, *Ion Exchange,* McGraw-Hill, New York, 1962.

12. D. J. H. Sandiford, *J. Appl. Chem.,* **8,** 188 (1958).

13. E. Bittencourt, V. Stannett, H. B. Hopfenberg, and J. L. Williams, *J. Appl. Polym. Sci.,* to appear.

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